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C–F Bond Activation of $P(C_6F_5)_3$ By Ruthenium Dihydride Complexes: Isolation and Reactivity of the 'Missing' $Ru(PPh_3)_3H$(halide) Complex, $Ru(PPh_3)_3HF$

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Abstract

The major product of the reaction between $Ru(IMe_4)_2(PPh_3)_2H_2$ (**1**; IMe_4 = 1,3,4,5-tetramethylimidazol-2-ylidene) and $P(C_6F_5)_3$ (PCF) is the 5-coordinate complex $Ru(IMe_4)_2(PF_2\{C_6F_5\})(C_6F_5)H$ **2**, which is formed via a complex series of C–F/P–C bond cleavage and P–F bond formation steps. In contrast, hydrodefluorination of all six *ortho* C–F bonds in PCF occurs with $Ru(PPh_3)_4H_2$ to afford $Ru(PPh_3)_3HF$ **3**. $NaBAr^F_4$ abstracted the fluoride ligand in **3** to give $[Ru(\{\eta^6\text{-}C_6H_5\}PPh_2)(PPh_3)_2H][BAr^F_4]$, while B_2pin_2 reacted with **3** in C_6D_6 to yield a mixture of $[Ru(\{\eta^6\text{-}C_6D_6)(PPh_3)_2H]^+$ and $Ru(PPh_3)_4H_2$. Treatment of **3** with HBpin (5 equiv) and $HSiR_3$ (R = Et, Ph; 2 equiv) afforded $Ru(PPh_3)_3(\sigma\text{-HBpin})H_2$ and $Ru(PPh_3)_3(SiR_3)_3H_3$ respectively. No stable substitution products were generated when **3** was reacted with Me_3SiX (X = CF_3, C_6F_5).

Introduction

Transition metal hydride complexes have proven to be valuable for effecting the cleavage of carbon-fluorine bonds.[1-11] In many cases, the precise mechanism(s) underpinning the C–F activation chemistry remain to be fully established.[12-18] However, based on examples where detailed mechanistic studies have been undertaken, the hydride ligands behave either innocently, for example, in undergoing elimination from the metal (in the case of dihydrides, through either thermally or photochemically induced reductive elimination) to generate coordinatively unsaturated metal species that then perform the C–F activation,[19,20] or, participate in a more active manner, for example, by undergoing insertion of fluorinated alkenes,[21,22] or by acting as nucleophiles to displace fluoride from C–F bonds in hydrodefluorination (HDF) reactions.[9,23-27]

In the last few years, we have reported that the *trans*-dihydride N-heterocyclic carbene (NHC) complexes $Ru(NHC)_2(PPh_3)_2H_2$ and $Ru(NHC)_4H_2$ (NHC = IMe_4, IEt_2Me_2, IMe_2)[28] exhibit the latter type of reactivity in the catalytic HDF of aromatic fluorocarbons.[29-31] In the course of a more general study on the reactivity of the mixed NHC/phosphine complex $Ru(IMe_4)_2(PPh_3)_2H_2$ (**1**, Scheme 1), we observed that both $P(C_6D_5)_3$ and $P(p\text{-}C_6H_4Me)_3$ readily displaced one or both of the PPh_3 ligands at room temperature.[32,33] In contrast, the chelating phosphines $Ph_2P(CH_2)_2PPh_2$ (dppe), $Ph_2P(CH_2)_3PPh_2$ (dppp) and $Ph_2PCH_2PPh_2$ (dppm) could only be substituted into **1** at elevated temperatures.[31] In an attempt to broaden the scope of these substitution reactions, we turned our attention to more electronically diverse phosphines, in particular, the perfluorinated phosphine, $P(C_6F_5)_3$ (abbreviated as PCF). While the chemistry of PCF (as well as its derivatives) with transition metal centers has been probed quite

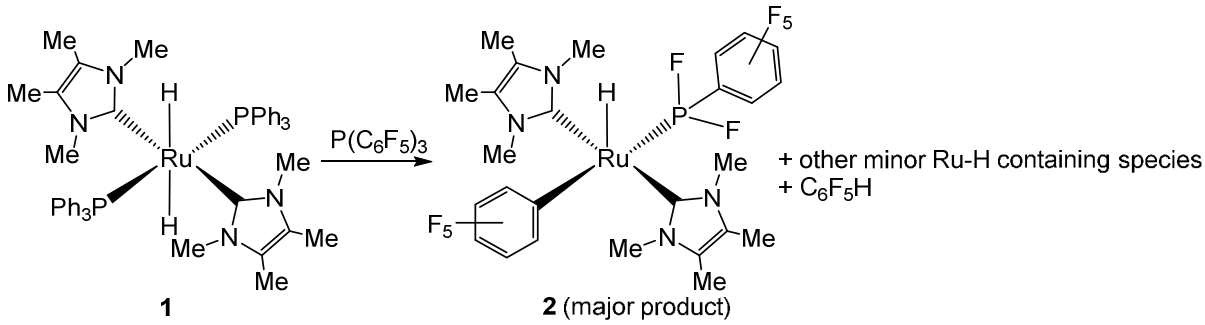
extensively, predominantly with catalytic applications in mind,[34-38] there are a small number of reports which show that PCF (or derivatives thereof) are susceptible to C–F activation by nucleophilic ligands on metal centers.[39-42] To the best of our knowledge, these nucleophilic ligands have not included hydrides.

Herein, we report that PCF undergoes a complex series of C–F/P–C bond cleavage and P–F bond formation processes with **1** to yield the unusual $PF_2(C_6F_5)$ complex, $Ru(IMe_4)_2(PF_2\{C_6F_5\})(C_6F_5)H$ (**2**). In contrast, hydrodefluorination of all six *ortho*-C-F bonds takes place with the tetrakis(triphenylphosphine) ruthenium dihydride complex, $Ru(PPh_3)_4H_2$, to yield $Ru(PPh_3)_3HF$ (**3**), the last of the well-known family of $Ru(PPh_3)_3H$(halide) complexes to be isolated.[43]

Results and Discussion

Synthesis and Characterization of $Ru(IMe_4)_2(PF_2\{C_6F_5\})(C_6F_5)H$ (2). The reaction of a C_6D_6 solution of **1** with 5 equiv PCF resulted in the loss of the Ru-H resonance in the ^{1}H NMR spectrum of **1** (δ - 6.54) over the course of ca. 24 h at room temperature to give one major metal hydride containing product **2** (the yield of **2** was ca. 70% determined by integration of all Ru-H signals in the ^{1}H NMR spectrum,), which appeared as a doublet of triplets signal at δ -29.62. This was characterized as the unusual 5-coordinate complex, $Ru(IMe_4)_2(PF_2\{C_6F_5\})(C_6F_5)H$, (Scheme 1) on the basis of 1- and 2-D NMR experiments using the wealth of spin ½ nuclei in the molecule (Figures S1-S7 in the Supporting Information). Thus, the ^{1}H NMR spectrum showed four methyl resonances in a ratio of 6:6:6:6 to 1 for the Ru-H signal, confirming the presence of two IMe_4 ligands and a single hydride. The low frequency of the Ru-H resonance was consistent with the hydride

being *trans* to a vacant coordination site, while the magnitude of the coupling constants ($^2J_{HP}$ = 46.1 Hz, $^3J_{HF}$ = 6.1 Hz) placed it *cis* to both the phosphine and ruthenium coordinated C_6F_5 ligands. The extremely unusual difluoro(pentafluorophenyl)phosphine $PF_2(C_6F_5)$,[44-46] which is, to the best of our knowledge, only known as a ligand in a single transition metal complex,[47] displayed a characteristic high frequency phosphorus resonance at 161 ppm. This appeared as a triplet of multiplets with a large one-bond triplet J_{PF} splitting of >1100 Hz.[48] The ^{19}F NMR spectrum revealed a similarly diagnostic high frequency (δ -31) resonance for the F_2P unit; this appeared as a doublet of triplets with a clearly resolved 1125 Hz doublet splitting to phosphorus. The 16 Hz triplet splitting was shown by ^{19}F COSY to originate from coupling to the two F atoms at the *ortho*-positions of the P-bound C_6F_5 group. The ^{19}F COSY spectrum allowed the signals for P- and Ru-bound C_6F_5 groups to be differentiated and fully assigned.



Scheme 1. Bond activation of PCF with **1**

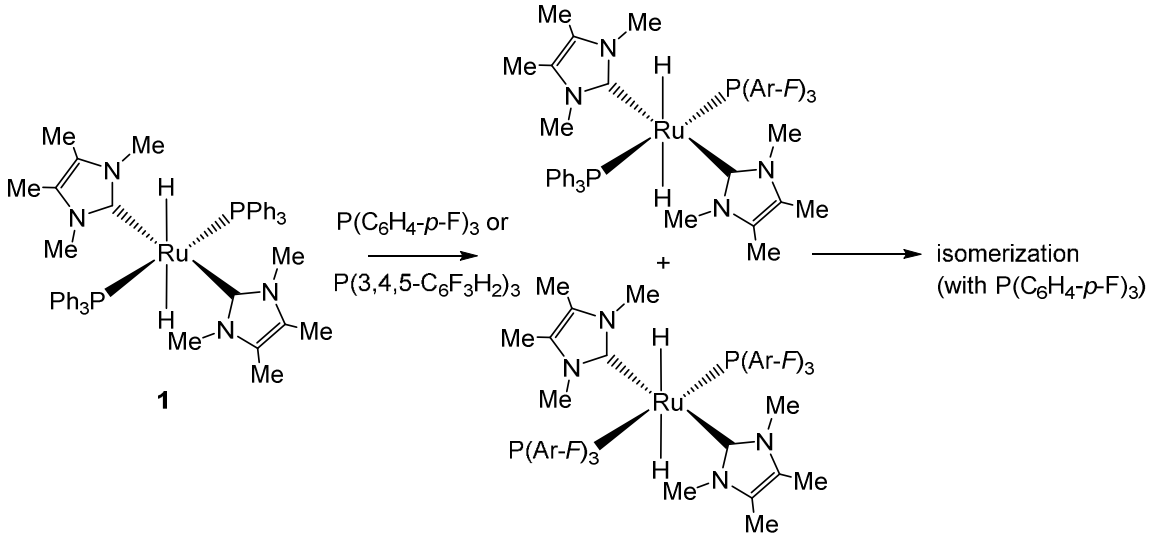
Given the unexpected structure of **2**, **1** was reacted with PCF under a range of conditions in an attempt to detect any reaction intermediates. A 1:1 mixture of **1** and PCF resulted in only incomplete conversion to **2** even after standing for 3 weeks at room temperature (after this duration, **1**:**2** were present in a 1:0.3 integral ratio; Figure S8 in the

Supporting Information). There were no NMR signals of any intermediates. Heating **1** and PCF in a 1:1.5 ratio at 50 ºC for ca. 24 h brought about complete loss of **1** and formation of **2** in ca. 60% yield by NMR spectroscopy; again no intermediate species were observed. Isolation of the reaction volatiles revealed only the presence of C_6F_5H. The ^{31}P NMR spectrum of the reaction residue showed signals for **2**, free PPh_3 and some unreacted PCF. Only signals of low intensity were present in the rest of the spectrum.

Despite exhaustive efforts, **2** could not be crystallized. Additionally, efforts to crystallize either a chloride derivative (by dissolution in CH_2Cl_2 or $CHCl_3$) or CO/isocyanide trapped derivative also met with failure. It is worth noting that in all of these reactions, $^{31}P/^{19}F$ NMR spectra showed that the $PF_2(C_6F_5)$ ligand remained intact.

Reactivity of 1 with Other Fluorinated Phosphines. The presence of $P(C_6F_5)$ groups appear to be mandatory for the bond activation steps described above. Neither $P(C_6H_4$-*p*-$F)_3$ nor $P(3,4,5\text{-}C_6F_3H_2)_3$[35] exhibited reactivity comparable to that of PCF with **1** (Figures S9 and S10 in the Supporting Information). Thus, addition of 2 equiv of $P(C_6H_4$-*p*-$F)_3$ to a C_6D_6 solution of **1** resulted in the slow (3 days) formation of two new triplet hydride resonances at slightly lower frequency (δ -6.71 and δ -6.89, both with $^2J_{HP}$ = 20.6 Hz) from that of **1**, which we propose arises from the substitution of one or two PPh_3 ligands by the fluorinated phosphine (Scheme 2). Over a prolonged period (ca. 3 weeks), further hydride signals appeared between ca. δ -8.3 and -9.1 and ca. δ -11.2 and -11.5. The similarity of these chemical shifts to those reported previously for isomers of **1**,[32] suggests that the initial mono- and bis-$P(C_6H_4$-*p*-$F)_3$ containing products also undergo isomerization over longer times.

The reaction between **1** and P(3,4,5-$C_6F_3H_2$)$_3$ led to rapid (1 h) and complete conversion to a single new species that exhibited a triplet hydride resonance at δ -6.79 ($^2J_{HP}$ = 20.9 Hz). Over an interval of weeks, this was slowly replaced by a new triplet Ru-H signal at δ -7.13 ($^2J_{HP}$ = 21.1 Hz). Following from the reactivity of P(C_6H_4-*p*-F)$_3$ above, these most likely represent mono- and bis-P(3,4,5-$C_6F_3H_2$)$_3$ substitution products. No isomerization was seen in this case at longer times.



Scheme 2. Substitution chemistry of **1** with P(C_6H_4-*p*-F)$_3$ and P(3,4,5-$C_6F_3H_2$)$_3$

Synthesis and Characterization of Ru(PPh$_3$)$_3$HF (3). The complex series of C–F and P–C bond cleavage steps, together with P–F and C–H bond formation,[49-53] necessary to generate Ru-$PF_2(C_6F_5)$ and Ru-C_6F_5 groups and C_6F_5H, in tandem with the lack of any observable intermediates, makes it impossible to propose a credible mechanism to account for the formation of **2**. We therefore decided to adopt an alternative approach, to see if PCF displayed related activation chemistry with different ruthenium hydride precursors. Treatment of $Ru(PPh_3)_4H_2$ with an excess of PCF (4 equiv) led to a change from a yellow suspension to a homogeneous red solution over ca. 2 h at room

temperature. ^{31}P NMR spectroscopy revealed the presence of unreacted PCF and complete loss of ruthenium starting material, but no obvious new product resonances. However, the low frequency region of the ^{1}H NMR spectrum did show the formation of a quartet resonance at δ -22.33, attributable to $Ru(PPh_3)_3HF$ (**3**, Scheme 3). The identity of **3**, which was isolated in ca. 80% yield as an air-sensitive red-orange solid, was established unequivocally by X-ray diffraction as shown in Figure 1. The P_{ax}-Ru-P_{ax} angle of 153.023(17)° is similar to that found in the chloride, bromide and iodide derivatives.[54,55] In contrast, the P_{eq}-Ru-X angle ranged from a value of 133.41(5)° in **3** to 116.428(13)° in $Ru(PPh_3)_3HBr$.[55] The Ru-F bond length (2.0652(12) Å) was comparable to values found in a range of other five- and six-coordinate ruthenium(II) fluoride complexes, such as *cis*-$Ru(dppp)_2F_2$ (2.056(3)/2.069(3) Å),[56] $Ru(PPh_3)_3(CO)HF$ (2.0986(15) Å),[57] $Ru(P^tBu_2Me)_2(CO)(=CF_2)HF$ (2.065(1) Å)[58] and $Ru(Ind)(SIMes)(P(O^iPr)_3)F_2$ (2.017(3)/2.035(4); Ind = 3-phenylindenylidene; SIMes = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene).[59]

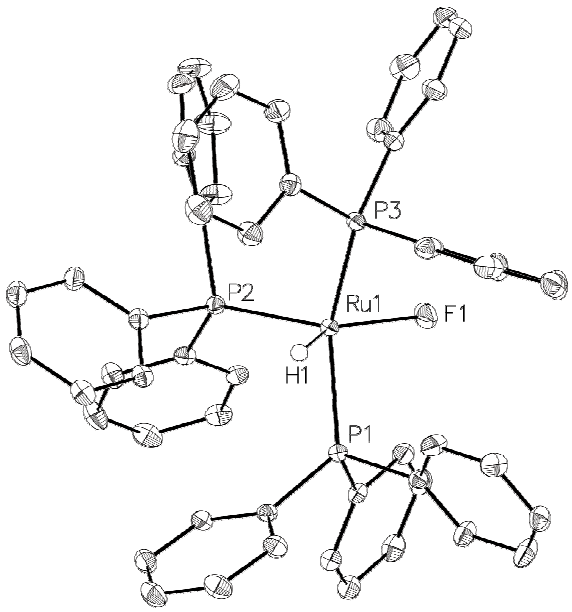


Figure 1. Molecular structure of $Ru(PPh_3)_3HF$ (**3**). Ellipsoids are shown at 30 % probability. Hydrogen atoms, with the exception of the Ru-H ligand are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)-F(1) 2.0652(12), Ru(1)-P(1) 2.3423(4), Ru(1)-P(2) 2.1996(5), Ru(1)-P(3) 2.3201(5), P(1)-Ru(1)-F(1) 88.19(4), P(2)-Ru(1)-F(1) 133.51(5), P(1)-Ru(1)-P(3) 153.023(17).

In many respects, **3** bears similarity to the recently reported rhodium fluoride complex $Rh(PPh_3)_3F$,[51d,e] in that they each represent the last member of the well-known families of $Ru(PPh_3)_3H$(halide) and $Rh(PPh_3)_3$(halide) complexes to be prepared. The solution fluxionality of $Ru(PPh_3)_3HX$ (X = Cl, Br, I)[43,60] was apparent in **3**. As the complex showed reasonable solubility across a range of solvents, variable temperature ^1H, ^{31}P and ^{19}F NMR spectra were recorded in toluene, THF as well as dichloromethane. Figure 2 shows representative examples of spectra; complete sets of spectra in all solvents are provided in Figures S11-S17 in the Supporting Information. At 298 K, the hydride resonance in **3** appeared as a quartet with $^2J_{HP}$ = 28.0 Hz in $C_6D_5CD_3$, THF-d_8 and CD_2Cl_2 (Figure 2a,b). This became a broad multiplet in CD_2Cl_2 at 199 K, whereas a more coupled multiplet was observed in both toluene and THF at the same temperature. The best resolved low temperature spectrum was measured in $C_6D_5CD_3$ at 199 K (Figure 2c); this simplified to a doublet with a $^2J_{HF}$ splitting of 16.0 Hz with ^{31}P decoupling (Figure 2d). While we were unable to observe any ^{31}P resonance in any solvent at room temperature, the 199 K $^{31}P\{^1H\}$ NMR spectrum recorded in $C_6D_5CD_3$ consisted of a 1:2 ratio of a doublet of triplets (δ 91; $^2J_{PF}$ = 84 Hz, $^2J_{PP}$ = 23 Hz) and a broadened triplet (δ 41; $J \approx 21$ Hz) (ESI). In all solvents across the temperature range 298-199 K, the Ru-F

resonance only ever appeared as a broad singlet, ranging in chemical shift from δ -190 to δ -205 (Figure 2e).[61]

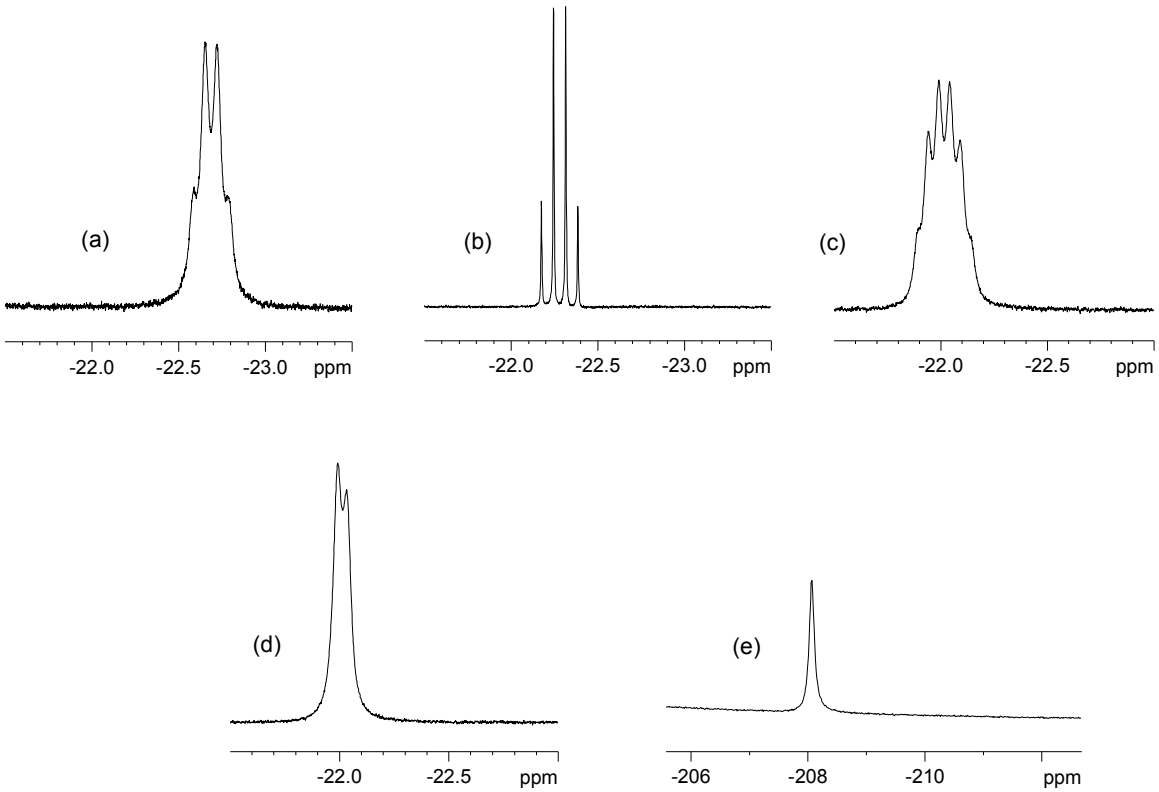
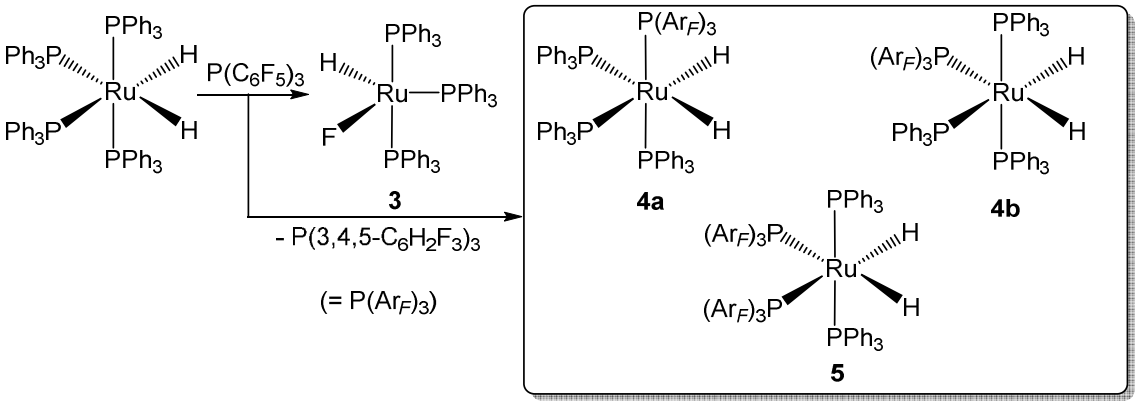


Figure 2. ^{1}H NMR spectrum (400 MHz) of Ru-H resonance of $Ru(PPh_3)_3HF$ **3** in (a) CD_2Cl_2 (298 K), (b) THF-d_8 (298 K), (c) $C_6D_5CD_3$ (199 K), (d) $^{1}H\{^{31}P\}$ NMR spectrum in $C_6D_5CD_3$ at 199 K. (e) ^{19}F NMR spectrum (376 MHz) of Ru-F resonance of **3** in THF-d_8 at 298 K.

Mechanism of Formation of 3. In contrast to the complex bond activation/formation steps involved in the formation of **2**, the formation of **3** arises by hydrodefluorination of PCF. This was probed by monitoring the reaction of different ratios of $Ru(PPh_3)_4H_2$:PCF by NMR spectroscopy. With sub-stoichiometric ratios of Ru:PCF (i.e. 6:1 and 9:1), we

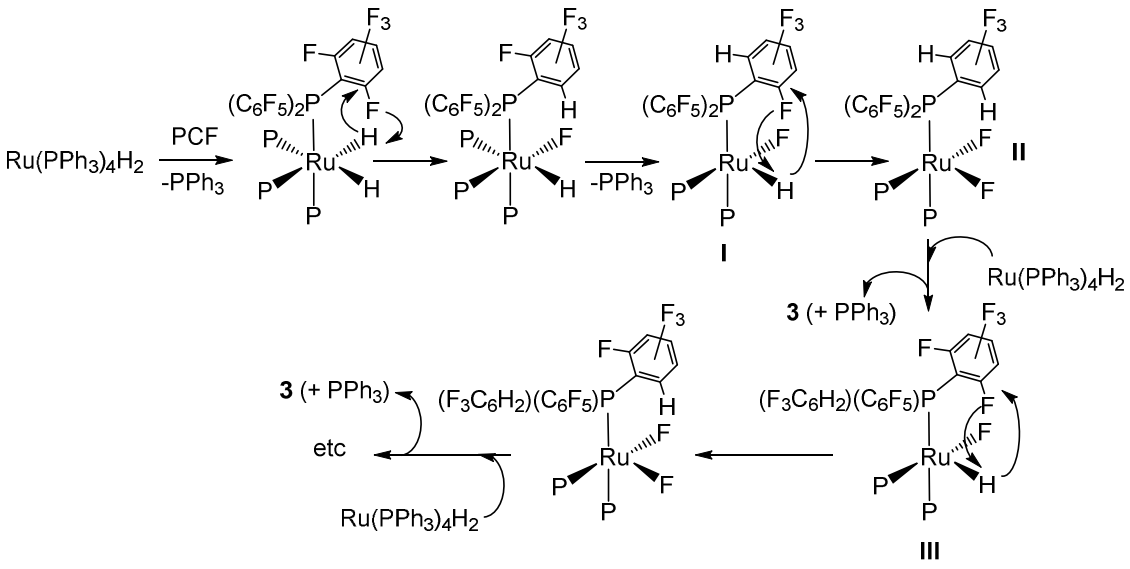
were able to observe three minor ruthenium containing products (**4a**, **4b** and **5**) in addition to **3** (Scheme 3 and Figure S19 in the Supporting Information). Each of these species showed two ^{19}F NMR signals (a doublet of doublets and a triplet of triplets, relative ratio of 2:1) at much higher frequency than the fluoride resonance of **3**, in a region of the spectrum associated with fluoroaromatic groups. A subsequent reaction of $Ru(PPh_3)_4H_2$ with $P(3,4,5\text{-}C_6F_3H_2)_3$ afforded the same three species, but no **3** (Figure S20 in the Supporting Information).[62] All four Ru species (**3**, **4a**, **4b** and **5**) can be rationalized by *ortho*-hydrodefluorination of PCF. The regioselectivity is consistent with a pathway involving substitution of PCF into $Ru(PPh_3)_4H_2$, followed by intramolecular nucleophilic attack by Ru-H at an *ortho*-C–F position. An analogous intramolecular attack of a Pt-OMe ligand has been proposed to account for the reaction of the *ortho*-C–F bonds in $[Pt(PPh_2C_6F_5)_2(THF)Me]$ with NaOMe to give $Pt(PPh_2\{2,6\text{-}(OMe)_2C_6F_3\})_2(OMe)Me$.[39,40] Very recently, Kayaki and co-workers[63] have reported that Ir-H complexes bearing fluorinated phenylsulfonyl-1,2-diphenylethylenediamine ligands undergo HDF at the *ortho*- C-F position to generate iridacycle products.



Scheme 3. Synthesis of **3** and proposed structures of **4a**, **4b** and **5**.[59]

The formation of the P(3,4,5-$C_6F_3H_2$)$_3$ complexes **4a**/**4b** and **5**, together with the lack of any signals for bound or free partially hydrodefluorinated phosphines (e.g. P(3,4,5-$C_6F_3H_2$)(C_6F_5)$_2$) implies that the HDF of all six available *ortho*-C-F sites in a molecule of PCF must be rapid, and certainly faster than the dissociation of any partially hydrodefluorinated phosphine. In the Pt chemistry above, Roundhill suggested that facile free rotation about the Pt-PR_3 bond allows all four *ortho*-fluorines to be placed very readily in close proximity to the reactive Pt-OMe group.

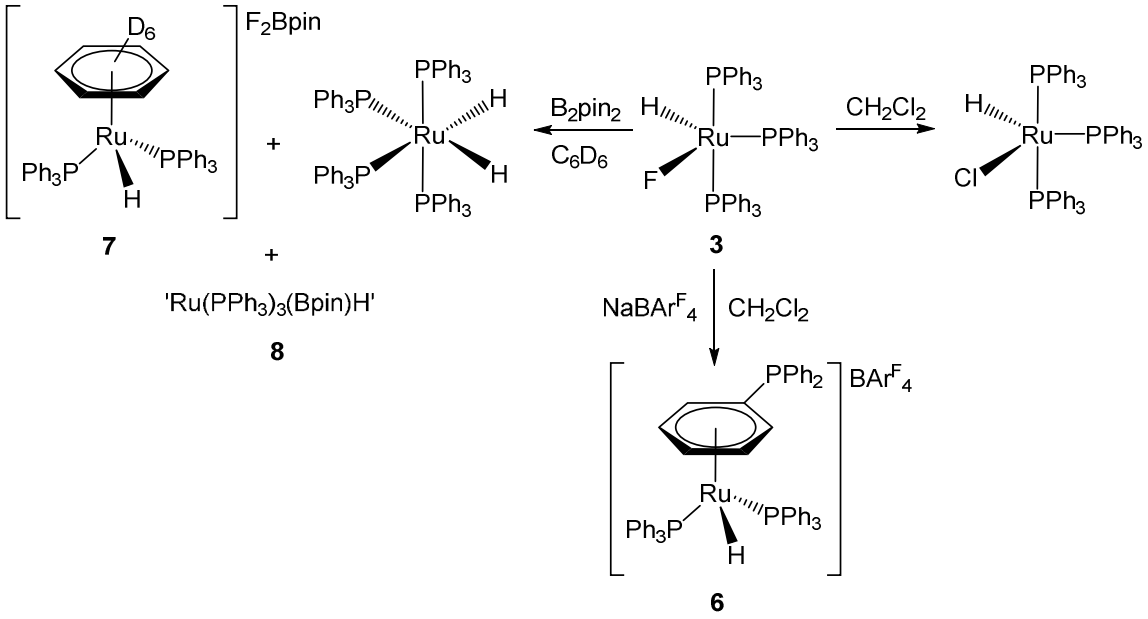
Scheme 4 shows a possible pathway to **3**. Initial intramolecular HDF at an *ortho*-C-F bond would yield the substituted hydride fluoride complex **I** (assumed to 5-coordinate like **3**), which could then bring about a second HDF step with formation of the difluoride complex **II**.[64,65] Comproportionation of **II** and $Ru(PPh_3)_4H_2$ (known for $[Ru(PPh_3)_2I_2]_2$ and $Ru(PPh_3)_4H_2$)[55] would then generate a reactive Ru-H ligand in **III**, allowing HDF to propagate until P(3,4,5-$C_6F_3H_2$)$_3$ is formed.



Scheme 4. Possible pathway for the intramolecular HDF of PCF to form **3**.

Reactivity of $Ru(PPh_3)_3HF$. As for other $Ru(PPh_3)_3HX$ complexes, **3** was stable in solution under inert conditions, but degraded rapidly upon exposure to air to afford green-black solutions. It proved to be relatively thermally robust in solution, with traces of new signals only apparent by ^1H NMR spectroscopy upon heating at 70 °C in THF-d_8 for ca. 7 h. Dissolution of **3** in CD_2Cl_2 afforded traces of $Ru(PPh_3)_3HCl$ within hours, although complete conversion required days at room temperature (Figure S23 in the Supporting Information). $Ru(PPh_3)_3HBr$ was formed in time of mixing upon addition of $C_6H_5CH_2Br$ to **3**, whereas reaction with bromodecane only occurred over several days. No reaction took place with PhI either at room temperature or at 70 ºC.

Treatment of **3** with $NaBAr^F_4$ in CH_2Cl_2 (Scheme 5) resulted in an almost near instantaneous disappearance of the starting material and formation of the $[BAr^F_4]$ salt **6** of the known cation $[Ru(\eta^6\text{-}C_6H_5PPh_2)(PPh_3)_2H]^+$, which was identified through the presence of a triplet of doublets Ru-H hydride resonance at δ -8.61, and two ^{31}P signals at δ 49.0 and -5.2 (Figure S24 in the Supporting Information).[66,67]

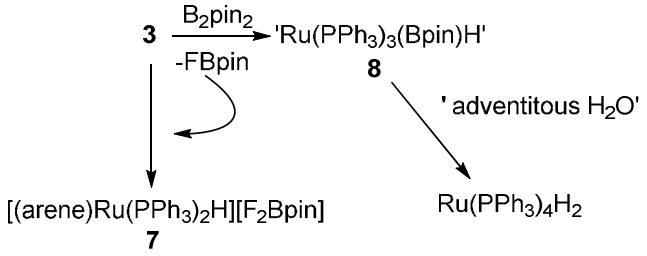


Scheme 5. Reactivity of **3**.

Reactivity of 3 with B_2pin_2 and HBpin. A ^{1}H NMR spectrum of a C_6D_6 solution of **3** recorded 5 min after the addition of 1 equiv B_2pin_2 showed residual starting material in an integral ratio of 1:0.2:0.4 to two new Ru-H containing products **7** and **8** with resonances at δ -5.49 and -9.33 respectively (Scheme 5; Figures S25-S27 in the Supporting Information). The chemical shift and coupling constant of **7** are consistent with those of the cation, $[(\eta^6\text{-arene})Ru(PPh_3)_2H]^+$ (δ -9.33; t, $^2J_{HP}$ = 36.7 Hz),[68] in which the arene is presumably C_6D_6. The presence of a broad $^{11}B\{^1H\}$ NMR triplet resonance ($^1J_{BF}$ = ca. 19 Hz) at δ 6.7, along with a broad ^{19}F resonance at ca. δ -141, indicates that $[F_2Bpin]^-$ is the accompanying anion.[69]

Within 30 min, an additional second-order hydride signal for $Ru(PPh_3)_4H_2$ appeared in the ^{1}H NMR spectrum at δ -10.16. This increased in intensity over time at the expense of **8**. After 1 h, **3** had been fully consumed and after ca. 2 h, **8** was also no longer present.

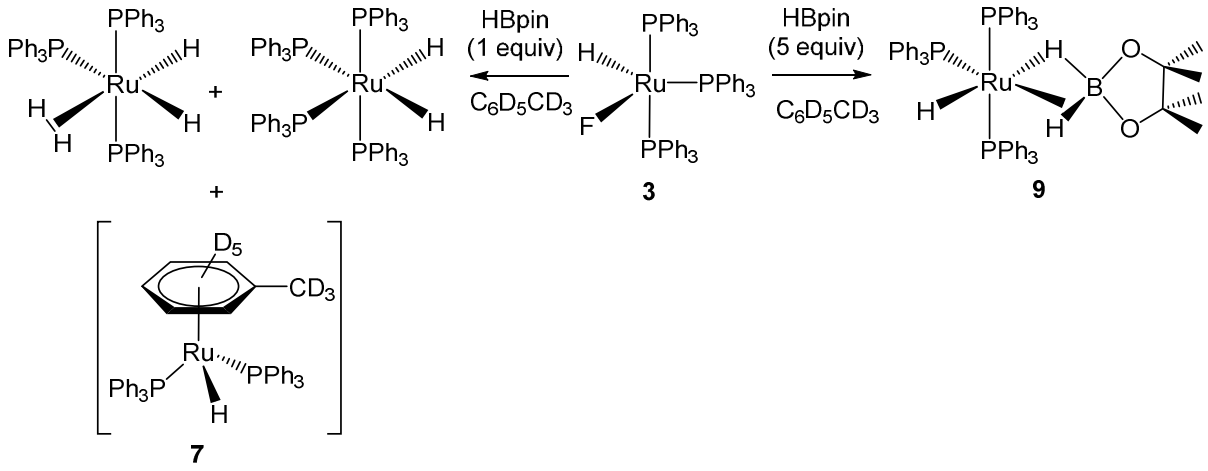
We propose that **8** is the hydride boryl complex, $Ru(PPh_3)_3H(Bpin)$.[70] Scheme 6 shows a possible pathway to the products from reaction with B_2pin_2. Initial formation of **8** releases FBpin, which could be trapped by **3** to give **7**. When the reaction was monitored quantitatively in the presence of an internal standard, all of the ruthenium was accounted for by the concentrations of **7** and $Ru(PPh_3)_4H_2$. However, mass balance of the Ru-H ligands requires some additional source of hydride. The presence of adventitious moisture (in solvent, on glassware, or in the sample of B_2pin_2) most likely accounts for this and also helps to rationalize the degradation of the boryl ligand in **8**.[71] There were only minor differences in the reaction profile upon changing the stoichiometry of the reaction. Thus, with just 0.5 equiv B_2pin_2, although **3** (unsurprisingly) took longer to be consumed, formation of **7**, $Ru(PPh_3)_4H_2$ and **8** was still observed at early times in the reaction, and **8** ultimately disappeared to leave just **7** and $Ru(PPh_3)_4H_2$.[72]



Scheme 6. Possible mechanism for the reaction of **3** and B_2pin_2.

The reaction of **3** with an equimolar amount of HBpin in toluene-d_8 gave the toluene analogue of **7** and $Ru(PPh_3)_4H_2$, but, in this instance, they were accompanied by formation of both the dihydrogen dihydride complex, $Ru(PPh_3)_3(\eta^2\text{-}H_2)H_2$[73,74] and free FBpin (Scheme 7; Figures S28 and S29 in the Supporting Information). The composition

of the reaction mixture changed over 2 days, to ultimately afford only $Ru(PPh_3)_4H_2$ and $Ru(PPh_3)_3(\eta^2\text{-}H_2)H_2$. However, when an excess of HBpin (5 equiv) was employed, quite different chemistry was observed (Scheme 7) with formation of the σ-borane dihydride complex, $Ru(PPh_3)_3(\sigma\text{-HBpin})H_2$ (**9**), along with a minor species discussed further below (Figures S30-S32 in the Supporting Information). Crystals of **9** suitable for X-ray diffraction (Figure 2) were obtained upon layering a C_6H_6 solution of the complex containing 10 equiv HBpin with pentane.



Scheme 7. Reactions of **3** with HBpin as a function of stoichiometry.

Analysis of key structural metrics in comparison to those of $Ru(PCy_3)_2(\eta^2\text{-}H_2)(\sigma\text{-HBPin})H_2$ support formulation as a σ-borane dihydride rather than hydroborate species.[75-77] Thus, there is a small, but significant, difference between the B1-H2 (1.36(2) Å) and B1-H1 (1.57(2) Å) distances, consistent with assignment of the former to σ-B-H and the latter to Ru-H···B. The orientation of the Bpin group (i.e. the [O, O]-B-Ru angle) has been promoted by Sabo-Etienne as being particularly diagnostic of the B-H coordination

mode.[76] Thus, in $Ru(PCy_3)_2(\eta^2\text{-}H_2)(\sigma\text{-}HBPin)H_2$, this angle is 170.0°, while the mixed σ-borane/dihydroborate species, $Ru(PCy_3)_2(\sigma\text{-}HBPin)(\eta^2\text{-}H_2Bpin)H$, has a corresponding angle of 171.5° for the borane and 177.5° for the dihydroborate; in **9**, the value is 170.05(16)°. The Ru-B distance of 2.1747(16) Å in **9** is also similar to that in $Ru(PCy_3)_2(\eta^2\text{-}H_2)(\sigma\text{-}HBPin)H_2$ (2.173(2) Å).

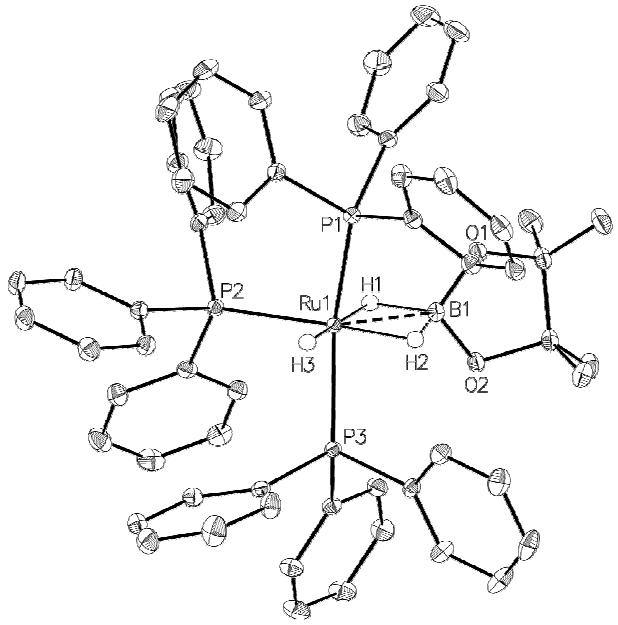


Figure 2. Molecular structure of $Ru(PPh_3)_3(HBPin)H_2$ (**9**). Thermal ellipsoids are shown at 30 % probability. Hydrogen atoms, with the exception those attached to Ru and B are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)-B(1) 2.1747(16), Ru(1)-P(1) 2.3337(4), Ru(1)-P(2) 2.3885(4), Ru(1)-P(3) 2.3398(4), P(1)-Ru(1)-P(2) 99.278(13), P(1)-Ru(1)-P(3) 152.859(13), P(2)-Ru(1)-P(3) 97.146(13).

Redissolved crystals of **9** gave a ^1H NMR spectrum comprising of three broad low frequency signals at δ -5.95, -8.03 and -10.52 in a 1:1:1 ratio at 298 K. At 259 K, the two lowest frequency resonances resolved into a triplet of doublets ($^2J_{HP}$ = 27.4, 16.6 Hz) and

a doublet of triplets ($^2J_{HP}$ = 58.7, 17.6 Hz) respectively. The signal at ca. δ -6 remained as a singlet, albeit much sharper. Additional low temperature NMR measurements showed that all three resonances (i) were unchanged in the 211 K $^1H\{^{11}B\}$ spectrum, but that they collapsed to singlets in the $^1H\{^{31}P\}$ spectrum at the same temperature, (ii) were all in exchange (EXSY, 259 K; Figures S32 in the Supporting Information) and (iii) correlated (^1H-^{31}P HMQC, 211 K) to a doublet (δ 52.2, $^2J_{PP}$ = 25 Hz) and a triplet (δ 50.5, $^2J_{PP}$ = 25 Hz)[78] in the $^{31}P\{^1H\}$ NMR spectrum. The multiplicities of the proton resonances at low temperature, together with the magnitudes of J_{HP}, allows clear assignment of the signals at room temperature at ca. δ -6, -8 and -10.5 to σ-B-H, Ru-H and Ru-H···B respectively. The respective T_1 values of 163 (378), 291 (865) and 191 (447) ms (259 K (values in parentheses measured at 211 K), 500 MHz) support these assignments. The ^{11}B NMR spectrum showed just single broad resonance at δ 21.9; in contrast to complexes described by Sabo-Etienne, this signal is on the lower frequency side of that for free HBpin.[76]

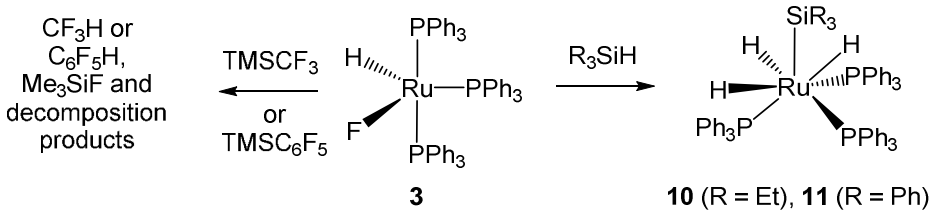
Proton NMR spectra of redissolved crystalline **9** showed the same minor product noted above that is observed in the initial reaction of $Ru(PPh_3)_4H_2$ with HBpin. This species displayed a multiplet Ru-H resonance at δ -9.49 (T_1 = 195 (259 K), 440 (211 K) ms at 500 MHz)[79] that correlated to a sharp ^{31}P singlet at δ 46. The identity of this complex remains unclear. Moreover, unless free HBpin was present in solution, the formation of $Ru(PPh_3)_3(\eta^2\text{-}H_2)H_2$ was also observed spectroscopically (Figure S33 in the Supporting Information). After 3 weeks in solution, the dihydrogen dihydride complex was the only remaining ruthenium species observable by ^1H NMR spectroscopy.

A preliminary investigation suggested that **3** reacted with catecholborane (5 equiv) in the same way, although less cleanly. The room temperature ^{1}H NMR spectrum featured a number of broad low frequency resonances, which upon cooling to 235 K, sharpened to reveal an obvious 1:1:1 set of signals at ca δ -4.7, -7.9 and -10.0 assignable to $Ru(PPh_3)_3(\sigma\text{-HBcat})H_2$. However, there were also quite a significant number of other low frequency signals; therefore, the reaction was not pursued further.

Reactivity of 3 with silicon reagents. 3 reacted rapidly with Me_3SiCF_3 (1 or 10 equiv, toluene or THF, in the absence and presence of CsF) to bring about complete disappearance of the Ru complex in less than 24 h. The presence of Me_3SiF, PPh_3, and CF_3H (Figures S34 and S35 in the Supporting Information), together with the absence of any new Ru containing species, suggested that conversion of **3** to $Ru(PPh_3)_3H(CF_3)$ may have taken place, but was followed by facile decomposition.[80] This is consistent with the paucity of Ru-CF_3 complexes in the literature.[81] Indeed, all of the examples that are known contain a π-accepting CO ligand and display a strong susceptibility to undergo α-F elimination to yield difluorocarbene complexes.[58, 82-84] The reaction of **3** with $Me_3SiC_6F_5$ (again over a range of solvents, in different stoichiometries and in the absence/presence of CsF) was much slower than with Me_3SiCF_3, but again failed to generate any new Ru-C_6F_5 containing products. Free C_6F_5H and $Ru(PPh_3)_4H_2$ were apparent as a result of decomposition (Scheme 8).

Addition of 2 equiv of R_3SiH (R= Et, Ph) to C_6D_6 solutions of **3** generated $Ru(PPh_3)_3(SiR_3)H_3$ (R= Et **10**, Ph **11**; Scheme 8) in the time of mixing (Figures S36-S39 in the Supporting Information). Both complexes were initially reported over 40 years ago following reaction of $Ru(PPh_3)_4H_2$ with the appropriate silane,[85,86] although their

characterization was limited to ^{1}H NMR/IR spectroscopy and elemental analysis. X-ray quality crystals of **10** were isolated upon slow evaporation of a THF solution of the complex, while those of the $SiPh_3$ analogue were isolated from benzene/hexane following the generation of **11** by reaction of $Ru(PPh_3)_4H_2$ and Ph_3SiH. The hydride ligands were located and refined without restraints in the molecular structure of **10**, whereas in **11**, they were located and refined, subject to being equidistant from Ru1 (Figure 3). As noted for other group 8 metal $ML_3(SiR_3)H_3$ complexes[87-92] there is an approximately tetrahedral arrangement of the SiP_3 units with the hydride ligands capping the SiP_2 faces.



Scheme 8. Reactions of **3** with silicon reagents.

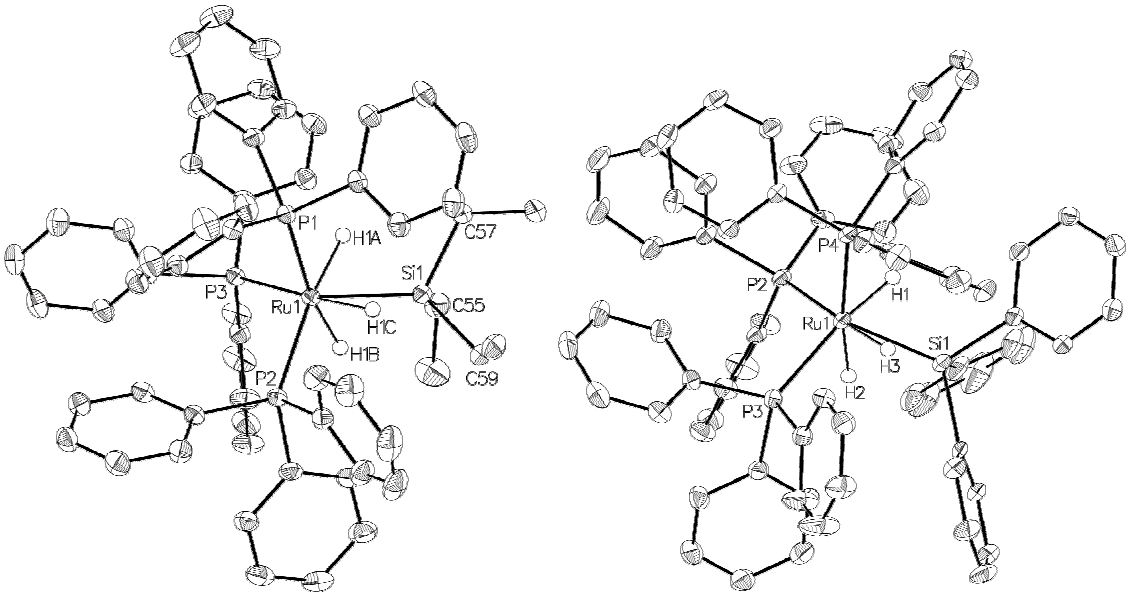


Figure 3. Molecular structures of $Ru(PPh_3)_3(SiEt_3)H_3$ (**10**, left) and $Ru(PPh_3)_3(SiPh_3)H_3$ (**11**, right). Ellipsoids are shown at 30 % probability. Hydrogen atoms (with the exception of those bound to Ru, as well as the disordered component of one phenyl ring attached to Si1 in **11**) have been omitted for clarity. Selected bond lengths (Å) and angles (°) for **10**: Ru(1)-Si(1) 2.4114(5), Ru(1)-P(1) 2.3969(4), Ru(1)-P(2) 2.4333(5), Ru(1)-P(3) 2.4043(4), P(1)-Ru(1)-P(2) 105.604(16), P(1)-Ru(1)-P(3) 102.854(15), P(1)-Ru(1)-Si(1) 112.757(17). **11**: Ru(1)-Si(1) 2.3682(16), Ru(1)-P(2) 2.4288(5), Ru(1)-P(3) 2.4332(6), Ru(1)-P(4) 2.4404(5), P(2)-Ru(1)-P(3) 104.980(18), P(2)-Ru(1)-P(4) 104.597(17), P(2)-Ru(1)-Si(1) 114.49(2).

Differentiating between silane and silyl hydride coordination modes remains the focus of much debate and discussion.[77,93-95] The shortest Si···H contact in **10** involves H1C, and at 2.02(2) Å, it is comparable to the values noted in $Ru(PMe_3)_3(SiMe_3)H_3$ (2.13 Å),[96] $Ru(PMe_3)_3(SiMe_2CH_2SiMe_3)H_3$ (2.00 Å)[97] and $Ru(IMe_4)_2(PPh_3)(SiPh_3)H_3$ (2.075

Å).[31] respectively. This suggests that **10** is best considered as a silyl trihydride complex which retains some degree of interaction between Si and $H_{hydride}$ centres. In line with this, the $^2J_{SiH}$ splitting (23 Hz) lies between 10 and 65 Hz, values proposed as representing the upper limit for M(Si)H and lower limit for M(σ-Si-H) species respectively.[77] The T_1 value of 300 ms (258 K, 400 MHz) for the hydride resonance in **10** rules out any non-classical dihydrogen interactions.[92]

Summary and Conclusions

Two very different products, $Ru(IMe_4)_2(PF_2\{C_6F_5\})(C_6F_5)H$ (**2**) and $Ru(PPh_3)_3HF$ (**3**), result from the reactions of the ruthenium dihydride complexes $Ru(IMe_4)_2(PPh_3)_2H_2$ and $Ru(PPh_3)_4H_2$ with tris(pentafluorophenyl)phosphine (PCF). The complexity of the C-F/P-C bond cleavage and P-F bond formation steps involved in the formation of **2**, together with the lack of observable intermediates on the reaction pathway, provide no obvious clues to the mechanism of the reaction, although it seems likely that the high nucleophilicity of the hydride ligands in $Ru(IMe_4)_2(PPh_3)_2H_2$ that results from the *trans* H-Ru-H geometry is an important feature of the overall process. The use of varying ratios of $Ru(PPh_3)_4H_2$ and PCF, as well as use of the partially fluorinated phosphine $P(3,4,5\text{-}C_6F_3H_2)_3$, provides good evidence that **3** is formed via an intramolecular attack of the Ru-H ligands to bring about hydrodefluorination of the *ortho*-C-F positions of a coordinated PCF ligand. **3** shows features of the well-known heavier halide analogues, particularly, the highly fluxional behavior in solution. In terms of reactivity, the fluoride ligand in **3** is readily displaced by boranes and silanes. Fifty years after Wilkinson's seminal report of

$Ru(PPh_3)_3HCl$,[43] we are delighted to have completed the family of known $Ru(PPh_3)_3H$(halide) complexes, albeit via an unanticipated reaction.

Experimental

General considerations

All manipulations were carried out using standard Schlenk, high vacuum and glovebox techniques using dry and degassed solvents. C_6D_6, $C_6D_5CD_3$ and THF-d_8 were vacuum transferred from potassium, while CD_2Cl_2 was distilled from CaH_2. NMR spectra were recorded at 298 K (unless otherwise stated) on Bruker Avance 400 and 500 MHz NMR spectrometers and referenced as follows: C_6D_6 (^{1}H, δ 7.15; ^{13}C, δ 128.0), $C_6D_5CD_3$ (^{1}H, δ 2.09; ^{13}C, δ 21.3), THF-d_8 (^{1}H, δ 3.58), CD_2Cl_2 (^{1}H, δ 5.32). ^{31}P{^{1}H} spectra were referenced externally to 85% H_3PO_4 (δ 0.0), ^{19}F spectra externally to $CFCl_3$ (δ 0.0). PPh_3 resonances are excluded unless they could be assigned unequivocally. Elemental analyses were performed by Elemental Microanalysis Ltd, Okehampton, Devon. $Ru(IMe_4)_2(PPh_3)_2H_2$ (**1**)[32] and $Ru(PPh_3)_4H_2$[98] were prepared according to literature methods.

$Ru(IMe_4)_2(PF_2\{C_6F_5\})(C_6F_5)H$ (2). $Ru(IMe_4)_2(PPh_3)_2H_2$ (17 mg, 0.019 mmol) and PCF (21 mg, 0.039 mmol) were combined with C_6H_6 (0.5 mL) in a J. Young's resealable NMR tube and the solution heated at 50 °C for 24 h. The deep-red solution was analysed by NMR spectroscopy and shown to contain 2 as the major product. ^{1}H NMR (C_6D_6, 500 MHz): δ 3.38 (s, 6H, NCH_3), 3.27 (s, 6H, NCH_3), 1.31 (s, 6H, NCCH_3), 1.24 (s, 6H, NCCH_3), -29.63 (dt, $^2J_{HP}$ = 46.1 Hz, $^3J_{HF}$ = 6.2 Hz, 1H, RuH). ^{31}P{^{1}H} NMR (C_6D_6, 202 MHz): δ 161.5 (tm, $^1J_{PF}$ = 1126 Hz). ^{19}F NMR (C_6D_6, 470 MHz): δ -31.1 (dt,

$^{1}J_{FP}$ = 1126 Hz, $^{4}J_{FF}$ = 16 Hz, 2F, PF_2), -114.5 (br m, 2F, Ru-*o*-C_6F_5), -137.3 (m, 2F, P-*o*-C_6F_5), -154.4 (t, $^{3}J_{FF}$ = 21 Hz, 1F, P-*p*-C_6F_5), 162.7 (m, 2F, P-*m*-C_6F_5), -163.1 (t, $^{3}J_{FF}$ = 20 Hz, Ru-*p*-C_6F_5), -163.4 (m, 2F, Ru-*m*-C_6F_5). Selected $^{13}C\{^{1}H\}$ NMR (125 MHz, C_6D_6):* δ 188.3 (d, $^{2}J_{CP}$ = 17 Hz, N*C*N), 124.3 (s, N*C*CH_3), 124.0 (s, N*C*CH_3), 34.5 (s, N*C*H_3), 33.4 (s, N*C*H_3), 8.7 (s, (s, NC*C*H_3), 8.0 (s, NC*C*H_3). *Signals from C_6F_5 groups were not assigned.

$Ru(PPh_3)_3HF$ (3). $Ru(PPh_3)_4H_2$ (300 mg, 0.26 mmol) and $P(C_6F_5)_3$ (48 mg, 91.1 μmol) were dissolved in C_6H_6 (2 mL) and stirred at 298 K overnight to afford a deep red solution. This was filtered by cannula and the filtrate layered with pentane to afford **3** as dark red crystals. Yield 203 mg (79%). ^{1}H NMR (THF-d_8, 500 MHz): δ 7.27 (t, J_{HP} = 7.8 Hz, 18H, PC_6H_5), 7.12 (t, J_{HP} = 7.4 Hz, 9H, PC_6H_5), 6.94 (t, J_{HP} = 7.6 Hz, 18H, PC_6H_5), -22.33 (q, $^{2}J_{HP}$ = 28.0 Hz, 1H, Ru*H*). ^{19}F NMR (THF-d_8, 376 MHz): δ -208.1 Anal. calcd (found) for $C_{54}H_{46}P_3Ru$: C 71.42 (71.80), H 5.11 (5.24).

Reaction of 3 with $NaBAr^{F}_{4}$. $Ru(PPh_3)_3HF$ (14 mg, 0.015 mmol) was combined with excess $NaBAr^{F}_{4}$ (34 mg, 0.038 mmol) in CD_2Cl_2 in a J. Young's resealable NMR tube. ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra recorded after ca. 30 min showed formation of $[Ru(\eta^{6}\text{-}C_6H_5PPh_2)(PPh_3)_2H][BAr^{F}_{4}]$ **6**. Diagnostic ^{1}H NMR (400 MHz, CD_2Cl_2): δ 6.64 (t, $^{3}J_{HH}$ = 5.9 Hz, 1H, $C_6H_5PPh_2$), 5.08 (t, $^{3}J_{HH}$ = 5.7 Hz, 2H, $C_6H_5PPh_2$), 4.41 (m, 2H, $C_6H_5PPh_2$), -8.61 (td, $^{2}J_{HP}$ = 38.6 Hz, $^{3}J_{HP}$ = 8.6 Hz, 1H, RuH). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 162 MHz): δ. 49.0 (s), -5.2 (s).

Reaction of 3 with B_2pin_2. C_6D_6 solutions of $Ru(PPh_3)_3HF$ (15 mg, 0.017 mmol) and B_2pin_2 (4 mg, 0.016 mmol), or $Ru(PPh_3)_3HF$ (16 mg, 0.018 mmol) and B_2pin_2 (2 mg, 0.008 mmol), were prepared in J. Youngs NMR tubes and the reactions monitored

by NMR spectroscopy. Spectra indicated the formation of [(η^6-C_6D_6)Ru(PPh_3)$_2$H][F_2Bpin] (**7**: ^{1}H NMR (C_6D_6, 500 MHz): δ -9.33 (t, $^2J_{HP}$ = 36.7 Hz, 1H, RuH); ^{31}P{^{1}H} NMR (C_6D_6, 202 MHz, 298 K): δ 51.8 (s); ^{11}B{^{1}H} NMR (C_6D_6, 160 MHz): δ 6.7 (br t, $^1J_{BF}$ = 19 Hz); ^{19}F NMR (C_6D_6, 470 MHz): δ -141 (br s)), Ru(PPh_3)$_4$H$_2$ (^{1}H NMR (C_6D_6, 500 MHz): δ -10.16 (m, 2H, RuH); ^{31}P{^{1}H} NMR (C_6D_6, 202 MHz): δ 49.3 (t, $^2J_{PP}$ = 14 Hz), 41.1 (t, $^2J_{PP}$ = 14 Hz)) and **8**, which is tentatively assigned as Ru(PPh_3)$_3$H(Bpin) (^{1}H NMR (C_6D_6, 500 MHz): δ -5.50 (dt, $^2J_{HP}$ = 59.9 Hz, $^2J_{HP}$ = 31.6 Hz, 1H, RuH); ^{31}P{^{1}H} NMR (C_6D_6, 202 MHz): δ 55.3 (d, J_{PP} = 15 Hz), 43.7 (t, J_{PP} = 15 Hz)).

Ru(PPh_3)$_3$(HBpin)H$_2$ (9). A C_6H_6 solution (0.5 ml) of **3** (15 mg, 16.5 μmol) and HBPin (24.0 μL, 0.16 mmol) was layered with pentane to afford a small amount of crystals of **9** over a period of ca. 2 weeks. Selected ^{1}H NMR ($C_6D_5CD_3$, 400 MHz, 259 K): δ 0.77 (s, 12H, Bpin), -5.95 (br s, 1H, B*H*), -8.04 (td, $^2J_{HP}$ = 27.8 Hz, $^2J_{HP}$ = 16.5 Hz, 1H, Ru*H*), -10.46 (dt, $^2J_{HP}$ = 59.6, $^2J_{HP}$ = 17.5 Hz, 1H, Ru*H*···B). ^{31}P{^{1}H} NMR ($C_6D_5CD_3$, 162 MHz, 259 K): δ. 52.2 (d, $^2J_{PP}$ = 25.0 Hz), 50.4 (t, $^2J_{PP}$ = 25.0 Hz). ^{11}B ($C_6D_5CD_3$, 128 MHz, 259 K): δ 21.9 (br s). Consistently high %C values precluded satisfactory elemental analysis for **9** from being determined (e.g. anal. calcd (found) for $C_{60}H_{59}BO_2P_3Ru$: C 70.85 (71.50), H 5.85 (5.75)).

Reaction of 3 with Me_3SiCF_3. Reactions were conducted at room temperature in J. Youngs resealable NMR tubes using (i) **3** (6.6 mg, 0.007 mmol) and Me_3SiCF_3 (10.7 μL, 0.015 mmol) in $C_6D_5CD_3$ or THF-d_8 or (ii) **3** (23 mg, 0.025 mmol) and Me_3SiCF_3 (7.6 μL, 0.051 mmol) in $C_6D_5CD_3$ or THF-d_8, both in the absence and presence of CsF (2.3 mg, 0.015 mmol). In all cases, ^{1}H and ^{19}F NMR spectroscopy showed formation of

CF_3H (^{1}H NMR ($C_6D_5CD_3$, 500 MHz): δ 7.23, q, $^2J_{HF}$ = 80.0 Hz; ^{19}F NMR ($C_6D_5CD_3$, 470 MHz): δ -79.2, d, $^2J_{FH}$ = 79.8 Hz; THF-d_8: ^{1}H (500 MHz): δ 6.89, q, $^2J_{HF}$ = 79.6 Hz; ^{19}F, δ -79.5, d, $^2J_{FH}$ = 79.6 Hz) and Me_3SiF ($C_6D_5CD_3$ (470 MHz) ^{19}F, δ -157.9, m; THF-d_8: ^{19}F, δ -158.2, m).

$Ru(PPh_3)_3(SiEt_3)H_3$ (10). 3 (34 mg, 0.038 mmol) and Et_3SiH (12 μL, 0.076 mmol) were shaken vigorously in THF-d_8 in a J. Young's resealable NMR tube for 2 h to give a pale orange solution. Pale yellow crystals of **10** were obtained upon slow evaporation of solvent. These were washed with pentane (3 x 0.5 mL) and dried in vacuo. Yield 13 mg (34%). ^{1}H NMR (THF-d_8, 400 MHz): δ 7.19-7.08 (m, 27H, PC_6H_5), 6.99-6.89 (m, 18H, PC_6H_5), 0.61 (t, $^3J_{HH}$ = 7.4 Hz, 9H, $SiCH_2CH_3$), 0.43 (q, $^3J_{HH}$ = 7.4 Hz, 6H, $SiCH_2CH_3$), -10.58 (m, 3H, RuH_3; ^{1}H{^{31}P} NMR: s, $^2J_{SiH}$ = 22.3 Hz; T_1 = 300 ms (258 K, 400 MHz)). ^{31}P{^{1}H} NMR (THF-d_8, 162 MHz): δ 41.8 (s). ^{29}Si-^{1}H HMBC (THF-d_8, 258 K): δ 3.3 (br s). Anal. calcd (found) for $C_{60}H_{63}P_3SiRu$: C 71.61 (71.32), H 6.31 (6.66).

$Ru(PPh_3)_3(SiPh_3)H_3$ (11). (a) Ph_3SiH (2 mg, 0.008 mmol) was added to a C_6D_6 solution of **3** (4 mg, 0.004 mmol) in a J. Youngs resalable NMR tube. ^{1}H and ^{31}P NMR spectroscopy showed complete conversion to **11** within 40 min. (b) **11** was generated on a preparative scale by slow addition of a C_6H_6 (2 mL) solution of Ph_3SiH (34 mg, 0.13 mmol) to a benzene (5 mL) solution of $Ru(PPh_3)_4H_2$ (100 mg, 0.087 mmol). The reaction mixture was left to stand overnight, after which time the color had changed from pale yellow to colorless. The solution was layered with hexane, which slowly precipitated at colorless crystals of **11** at room temperature (40 mg, 80% yield). Selected ^{1}H NMR (C_6D_6, 500 MHz): δ -9.37 (m, 3H, RuH_3). ^{31}P{^{1}H} NMR (C_6D_6, 202 MHz): δ 37.5 (s). Anal. calcd (found) for $C_{72}H_{63}P_3SiRu$: C 75.17 (75.16), H 5.52 (5.82).

X-ray crystallography. Data for compounds **3**, **9**, **10** and **11** were obtained using an Agilent SuperNova instrument and a Cu-Kα source. These crystallographic experiments were conducted at 150 K, with the exception of that for **10** (for which data were garnered 200 K). All structures were solved using Olex2[99] and refined using SHELXL.[100] Refinements were uneventful in the main. The only additional points of note include the fact that the asymmetric units in **3** and **9** each housed one molecule of the ruthenium complex and one guest molecule of benzene. The hydride ligands were located in both cases, and while H1 in **3** was refined at a distance of 1.6 Å from Ru1, those in **9** were refined without restraints. In **10**, the asymmetric unit was seen to contain one molecule of the complex, and two molecules of THF. The hydrides in the main feature were readily located and refined without restraints. One of the solvent molecules was treated with the Olex2 solvent mask algorithm, as it is heavily disordered. The second solvent entity exhibited disorder of O1 and C6 therein, in a 50:50 ratio. The assignment of the oxygen is somewhat tentative as, ultimately, fractional occupancy atoms O1 and O1a were restrained to having similar anisotropic displacement parameters (ADPs) in the final least-squares, to assist convergence. The asymmetric unit in **11** was seen to comprise one molecule of the complex and three regions of solvent, which amounted to 2.5 molecules of benzene. The hydride ligands in the main feature were located and refined, subject to being equidistant from Ru1. The phenyl ring based on C13 (attached to Si1) was seen to be disordered in equal proportions over two proximate sites and the associated Si–C13/C13A distances were restrained to being similar in the final least–squares. Two of the solvent regions required disorder modelling. In particular, the one total benzene moiety based on C72 was modelled for disorder over two regions in a 50:50

ratio, while that based on C82 was disordered over three overlapped regions in a 40:40:20 ratio. The arising five, fractional occupancy rings in these 2 regions were refined as rigid hexagons, and ADP restraints were also included, to assist convergence. The half molecule of benzene present, at half occupancy (C88–C90) is located proximate to an inversion center which serves to generate the remainder of that entity.

Crystallographic data for all compounds have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 1849162-1849165 for **3**, **9**, **10** and **11** respectively. Copies of these data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax(+44) 1223 336033, e-mail: deposit@ccdc.cam.ac.uk.

Supporting Information Available: Multinuclear NMR spectra for complexes **2-11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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^{19}F NMR spectrum recorded in toluene-d_8, but in CD_2Cl_2, the Ru-F resonance sharpened to yield an obviously coupled, but still unresolvable, broad multiplet. In the $^{19}F\{^1H\}$ NMR spectrum, this became a broadish quartet with $^2J_{FP}$ = 40 Hz. Interestingly, the CsF also impacted on the appearance of the Ru-H signal in CD_2Cl_2 (there was no effect in toluene); rather than a quartet, a signal of higher multiplicity was now apparent, which became a broadish doublet with $^2J_{HF}$ = 13.1 Hz upon ^{31}P decoupling (see Figure S18 in Supporting Information). Addition of excess PPh_3 to each of these sample made no impact upon the appearance of either the ^1H or ^{19}F NMR spectra in dichloromethane, but in toluene, a more coupled (albeit still broad) Ru-H signal was apparent in the proton NMR spectrum, while the Ru-F signal tended towards a broad quartet in the $^{19}F\{^1H\}$ spectrum.

(62) The presence of three ^{31}P NMR signals (δ 62.1 (br dt, $^2J_{PP}$ = 239 Hz, $^2J_{PP}$ = 18 Hz), 43.8 (dt, $^2J_{PP}$ = 239 Hz, $^2J_{PP}$ = 16 Hz), 38.5 (dd, $^2J_{PP}$ = 18 Hz, $^2J_{PP}$ = 16 Hz)), together with a second-order Ru-H resonance (almost coincidental with that for $Ru(PPh_3)_4H_2$) for **4a** suggests it is formed upon substitution of $P(3,4,5\text{-}C_6F_3H_2)_3$ into an axial site of $Ru(PPh_3)_4H_2$. **4b** showed two multiplet Ru-H signals (δ -8.8 and -10.8) which simplified to a 1:1 ratio of two doublets ($^2J_{HH}$ = 8.4 Hz) upon ^{31}P decoupling, suggestive of an equatorially substituted isomer. **5**, which was was only ever observed at very low concentrations, is tentatively assigned as the bis-equatorially substituted complex, $Ru(PPh_3)_2\{P(3,4,5\text{-}C_6F_3H_2)_3\}_2H_2$, on the basis that it grows in intensity with time in both of the 9:1 and 6:1 reactions (Figures S20-S22 in the Supporting Information).

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(64) Attempts to prepare $Ru(PPh_3)_3F_2$ by heating **3** with $Et_3N{\cdot}3HF$, $C_6F_5CF_3$ or PCF were unsuccessful, with unreacted **3** remaining in all cases.

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(71) In line with this, as **8** degrades, we observe the formation of a new ^{11}B NMR signal at ca. δ 22, consistent with the formation of $(Bpin)_2O$. Bontemps, S.; Vendier, L.; Sabo-Etienne, S. *Angew. Chem. Int. Ed.* **2012**, *51*, 1671-1674

(72) Hexane precipitation from a benzene solution of **7** and $Ru(PPh_3)_4H_2$ allowed separation of the two components. NMR spectra of the isolated colorless precipitate of **7** redissolved in CD_2Cl_2 showed the same δ -9.08 triplet hydride resonance for the cation , but now the $[F_2Bpin]^-$ anion appeared in the $^{11}B\{^1H\}$ NMR spectrum as a very sharp triplet ($^1J_{BF}$ = 20.8 Hz) at δ -5.1 and as a 1:1:1:1 quartet with the same coupling at δ -144.4. Over a period of 10 days in solution, $[F_2Bpin]^-$ appeared to convert into a second, unknown anion, which showed a sharp quartet boron signal at δ -0.5 with J_{BF} = 9.6 Hz, the corresponding 1:1:1:1 quartet being at δ -146.3 in the ^{19}F NMR spectrum.

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(79) This signal was in a ca. 1:1:1:1 ratio with the three low frequency resonances of **8**.

(80) $^{1}H/^{19}F$ NMR monitoring of a cold (233 K) 1:2 mixture of **3**:$TMSCF_3$ showed signals for just the two initial reagents up to 298 K, at which point, CF_3H began to appear.

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C–F Bond Activation of $P(C_6F_5)_3$ By Ruthenium Dihydride Complexes: Isolation and Reactivity of the 'Missing' $Ru(PPh_3)_3H$(halide) Complex, $Ru(PPh_3)_3HF$

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$P(C_6F_5)_3$ undergoes C–F and P–C activation, as well as P–F bond formation, with the N-heterocyclic carbene complex, $Ru(IMe_4)_2(PPh_3)_2H_2$, to generate the unusual $PF_2(C_6F_5)$ complex, $Ru(IMe_4)_2(PF_2\{C_6F_5\})(C_6F_5)H$, whereas the reaction with $Ru(PPh_3)_4H_2$ leads to C–F activation and C–H formation to yield $Ru(PPh_3)_3HF$.